Synthesis and photocatalysis study of multiwalled carbon nanotubes grown in a lead-based microspherical support


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Abstract
Plumbonacrite films were used as support material for growth of carbon nanotubes and the resulting nanocomposite was tested as photocatalysts for the degradation of methylene blue dye. The plumbonacrite films were deposited on silicon substrates by a simple alkaline chemical bath deposition process. After the CNT growth process, the resulting nanocomposite samples were analyzed by X-ray diffraction, Raman spectroscopy and scanning electron microscopy. The high temperature during the CNT growth process decomposed the plumbonacrite material into lead microspheres, which were covered by the CNT constituting the nanocomposite films. Afterwards, the nanocomposite films were applied for the photodegradation of methylene blue molecules using natural sunlight. The nanocomposite films were reused for up to three cycles obtaining efficiencies in the degradation of the dye superior to 92% and a first order kinetics with rate constants of $8.9 \times 10^{-3}$ min$^{-1}$ in a maximum irradiation time of 240 minutes.

1. Introduction
One of the most studied materials in the recent years has been the multi and single-walled carbon nanotubes (CNTs).\textsuperscript{[1–3]} Due to their excellent physical, chemical and structural properties the application of these materials in different fields like catalyst, medicine, energy and electronics has been the focus of intensive research.\textsuperscript{[4–6]} There are different methodologies for the synthesis of CNTs such as arc-discharge,\textsuperscript{[7]} laser ablation,\textsuperscript{[8]} thermal deposition\textsuperscript{[9]} and chemical vapor deposition (CVD).\textsuperscript{[10,11]} Among the different synthesis processes, the CVD methodology has been widely used because of its high yield and low cost.\textsuperscript{[12–16]} This process involves the decomposition of a carbon-based material over metallic nanoparticles of Fe, Co and/or Ni, where the carbon accumulates and begins to form the characteristic tubular structure of the CNT.\textsuperscript{[17,18]} The metallic nanoparticles are previously deposited on different support materials like quartz,\textsuperscript{[19]} silicon,\textsuperscript{[20–22]} silicon carbide,\textsuperscript{[23]} silica,\textsuperscript{[24]} alumina \textsuperscript{[24]} or zeolites.\textsuperscript{[25]} The support material, its surface morphology and textural properties greatly affect the yield and quality of the resulting CNTs. That is why the search for new support materials for the synthesis of CNTs is of great current scientific and technological interest. On the other hand, CNTs, by themselves, are considered as a good support material for catalysts, due their large surface area and electronic properties.\textsuperscript{[26–28]} A significant number of papers have been published on the synthesis and applications of CNTs/semiconductor composites to act as photocatalyst for some chemical reactions, especially for the decontamination of organic pollutants in water.\textsuperscript{[29–34]} Furthermore, it has been reported that pure CNTs are effective for the photocatalytic degradation of H$_2$O$_2$ under visible light irradiation.\textsuperscript{[35]} This photocatalytic ability of CNTs was assigned to the large number of defects created during the growth process.

Plumbonacrite (Pb$_{10}$O(OH)$_6$(CO$_3$)$_6$) is a complex lead salt, product of lead corrosion, which can be obtained as thick films on different types of substrates by means of chemical bath deposition. The chemically deposited plumbonacrite films\textsuperscript{[36]} show a surface morphology highly texturized with thin hexagonal plates randomly oriented or arranged in flower-like structures, depending on the chemical formulation to obtain them.\textsuperscript{[36,37]} Our group has shown that plumbonacrite is a versatile material because its chemical groups bonded to lead, can be easily exchanged by chalcogenide ions to obtain lead chalcogenide semiconductor materials such as PbSe\textsuperscript{[38,39]} and PbTe.\textsuperscript{[40]} The ion exchange process can be done by either immersing plumbonacrite films in aqueous solution with chalcogenide ions at room temperature or exposing the film to a flux of hot chalcogenide gas. Lead oxide films can also be obtained from plumbonacrite films by just heating in air at high temperature. Some research works have reported that...
materials doped or mixed with Pb have good photocatalytic activities for the decomposition of organic compounds like methylene blue\cite{41} or perfluorooctanoic acid.\cite{42} Currently carbon-based materials are also used to obtain composite materials used as photocatalysts for water treatment\cite{43-45}. As it is known, the nanomaterials used as adsorbents to remove organic contaminants from water have been highly successful. This is due to their high porosity characteristics, a large active surface with greater number of active sites for interaction with different chemical species, ease of ionic exchange and high affinity for certain molecules. The nanoadsorbents not only work very fast but also allow to work with a much smaller amount of catalyst to carry out a process of adsorption and degradation, which leads to a reduction of the cost in the treatment of contaminated water. Among the various adsorbents based on nanomaterials, carbon-based materials have been tested as superior adsorbents for the removal of inorganic and organic pollutants.\cite{44,46-50} The incorporation of nanoadsorbents in other support materials improves the efficiency in the removal of inorganic metallic compounds and the degradation of organic ones, avoiding the loss of the nanomaterials, which is one of their major disadvantages. The development of this type of nanomaterials can be of significant relevance to address the growing problem related to the pollution of water produced by the human activity. Particularly, those produced by dyes contained in waste water from textile industry.

In this work, we report the growth of CNTs on plumbonacrite films as a novel support material and the photocatalytic activity of the resulting CNT/Pb nanocomposite films. The plumbonacrite films were deposited on silicon substrates by using an easy CBD process reported previously by our group and the films were transferred to a CVD reactor for the growth of CNTs. The photocatalytic efficiencies of MWCNTs/Lead-based microspherical composite films were evaluated in the degradation of methylene blue solutions. The results show that the nanocomposite films have strong photocatalytic activity for the degradation of methylene blue, and therefore they are promising high-performance photocatalyst for water decontamination.

2. Experimental

2.1. Materials

All the reagents were purchased in Sigma-Aldrich and were used as received. The used gases were bought in Infra Company. For the preparation of the plumbonacrite films sodium citrate dihydrate (99% purity), lead acetate trihydrate (99.5% purity) and potassium hydroxide (85% purity) were used. Cobalt nitrate hexahydrate (98% purity) and iron nitrate nonahydrate (98% purity) were used to prepare the catalyst for the carbon nanotubes. Finally, for the carbon nanotubes growth were used gases of N₂ (99.99%), N₂/H₂ (90%/10%) and C₂H₂ (98%).

2.2. Characterization

X-ray diffraction (XRD) technique was employed to study the crystalline structure of the support plumbonacrite material before and after the carbon nanotubes growth process, using a Rigaku DMax 2100 X-ray Diffractometer. Raman spectroscopy with a Labram-Dilor II micro–Raman spectrometer was used to confirm the obtaining of CNTs, using the 488-nm blue line as the excitation source. The morphology of the support material and CNTs was analyzed with a Jeol JXA-8530F Field Emission Electron Probe Microanalyzer. For the photocatalytic experiments an Ocean Optics Uv-Visible Absorption Spectrometer and a photoluminescence (PL) Jobin Yvon Horiba Spectrofluorimeter Model Fluoro Max-3 (excitation wavelength of 500 nm) were used.

2.3. Plumbonacrite synthesis

The plumbonacrite films were deposited on halves of 3-inch silicon wafer substrates by immersion in a 100 ml reactive solution containing the mixture of 0.2 M lead acetate, 0.4 M sodium citrate, 0.5 M potassium hydroxide and deionized water. Afterwards, in order to accelerate the CBD process, the reaction solution was exposed to irradiation from a UV lamp (364 nm, 22W) inside a closed box. The photo-induced chemical bath deposition process was realized at room temperature for 5 hours, after which a white, homogeneous and dense plumbonacrite layer is formed on the silicon substrate. Then, it was removed from the solution and dried with nitrogen.

2.4. Carbon nanotubes growth

The catalyst for the carbon nanotubes growth was made with a combination of Fe-Co 3:1 in weight relation.\cite{13,51} Iron and cobalt nitrates were dissolved in a solution of water:ethanol under magnetic stirring for 15 minutes. Then, 1 ml of the Fe-Co solution was placed on the plumbonacrite film deposited on the silicon substrate and let it dry at room temperature. After drying, the plumbonacrite film is placed in the center of a tubular furnace for the CNT growth process as reported in others works.\cite{52} The furnace was heated to 700°C (heating ramp of 20°C/min) under an inert atmosphere (N₂), after that, a N₂/H₂ gas was introduced at a rate of 2L/min for a total time of 30 min. Once completed this step, the pressure in the furnace was reduced to reach a vacuum of 200 mmHg and subsequently, acetylene diluted with nitrogen in a ratio of 20/80 v/v wash was introduced as a precursor gas for the growth of CNTs. Finally, after 30 minutes, the acetylene gas flow was stopped and the furnace was cooled to room temperature in an inert atmosphere. With the aim of analyzing the effect of the catalyst, a plumbonacrite film without catalyst on its surface was also introduced in the furnace, next to the plumbonacrite + FeCo catalyst.

2.5. Photocatalytic experiments

The resulting sample from the NTCs growth by CVD was applied as photocatalyst to degrade methylene blue (MB) under sunlight irradiation (20°43’ 20’ N, 100°28’ 10’ W, 1820 m above sea level). For this a 50 ml of 0.02 mM MB solution was poured in 150 ml beakers, then the CNTs/Plumbonacrite/Si sample was placed in the bottom of the
beaker. The beaker was placed under sunlight irradiation, and aliquots of the MB solution were taken after 30, 60, 90, 120, 180, and 240 min; these aliquots were analyzed with the UV-Vis absorption spectrometer and the spectrofluorometer. The nanocomposite films were used for 3 consecutive days in the photocatalysis experiments, each day with a new MB solution, and all the experiments were run simultaneously in duplicate. The concentration of MB in the solutions, \( C \), was measured as the maxima in the absorption spectra. The discoloration percentage of the MB solution, \( D \), was calculated with the next equation \(^{[53,54]}\):

\[
D = \frac{C_0 - C}{C_0} \times 100\%
\]

and the concentration of the MB in the solution as a function of the interaction of the dye solution with the photocatalysts, \( t \), was fit to the Langmuir-Hinshelwood kinetic model\(^{[55,56]}\) according to which the photocatalytic process can be expressed by the following first-order equation:

\[
\ln \frac{C_0}{C} = k_{app} t
\]

where \( k_{app} \) is the kinetic rate constant. The photocatalytic effect of isolated CNTs, grown through the same route, was studied in order to observe the effects provoked by the Pb-based support material.

### 3. Results and discussion

#### 3.1. Structural results

Figure 1 shows photographs of the plumbonacrite support material at different steps of the CNTs growth process. Figure 1a displays the plumbonacrite film grown on the silicon substrate where it is observed the formation of a white layer on the piece of the gray silicon wafer. The image in Figure 1b shows the plumbonacrite film impregnated with the Fe-Co catalyst solution. Here, the plumbonacrite film takes a reddish color due to the reaction with the Fe-Co solution. Finally, in the image 1c, the CNTs produced over the plumbonacrite film after the CVD process is shown. It can be observed that the plumbonacrite film with Fe-Co catalyst is now completely covered by a dense layer of CNTs with their characteristic black color.

Figure 2 shows the XRD patterns of a) the as-deposited plumbonacrite film before the CNTs growth process, the plumbonacrite film after the CNTs growth process b) without and c) with Fe-Co catalyst. At the bottom, the XRD pattern of the plumbonacrite film displays peaks which match with the lead oxide carbonate hydroxide crystalline phase (JCPDS 19–0680). This is a hexagonal crystalline structure with major diffraction peaks at 20.83°, 26.50°, and 34.29° related to the (112), (115) and (300) crystalline planes of this phase. The pattern 2b shows diffraction peaks of lead (JCPDS 04–0686) at 31.30°, 36.26°, 52.22°, 62.11°, and 65.23° corresponding to the (111), (200), (220), (311) and (222) planes of this cubic structure. Likewise, three additional peaks are observed at 28.63°, 31.83°, and 48.59° that correspond to the (101), (110), and (112) planes of...
the lead oxide phase, litharge (JCPDS 05–0561). This result indicates that due to the high temperatures and gases used during the CNTs growth process, plumbonacrite loses the hydroxide and carbonate groups to become lead oxide at 500°C, as it is reported in the literature,[57] and into lead at 700°C. The lack of diffraction signals related to CNTs in this pattern shows that CNTs did not grow on this sample because no catalyst was used during the growth process. After CNTs growth process, the XRD pattern of the resulting sample in 2c, displays an intense signal at 26.2° that correspond to the (002) diffraction signal from graphitic walls of the carbon nanotubes[58] (JCPDS 75–1621), which confirms the formation of carbon nanostructures in this sample. Two peaks corresponding to the signals of the (110) and (330) crystalline planes of FeCo alloys can be also observed at 43.87° and 44.72° (JCPDS 51–0740 and 48–1817, respectively). Furthermore, weak peaks associated to (200) and (110) diffraction signals of lead oxide and lead, respectively are observed in this pattern. This result suggests that the original plumbonacrite layer impregnated with the catalyst transformed also into lead oxide and lead after the CNTs growth process. The interlayer spacing of the graphitic walls $d_{002}$ was calculated from the XRD measurements employing the Bragg's law and the result was $d_{002} = 0.34219$ nm. The degree of graphitization $(g)$ was calculated based on the Maire and Mering formula[59]:

$$
g(\%) = \frac{0.3440nm - d_{002}}{0.3440nm - 0.3354nm} \times 100
$$

where $d_{002}$ is the interlayer spacing of the (002) diffraction planes, 0.303440 nm is the interlayer spacing of the non-graphitized carbon and 0.3354 nm is the interlayer spacing of an ideal type graphite crystallite. The equation is a relation between the obtained interplanar space and the ideal type graphite crystallite, the obtained value was $g = 21.04\%$. Similar results were reported by Narinder Kaur et al.[60] The graphitization can increase if the temperature of the growth process is increased according to R. Andrews and et al.[61]

The Raman spectrum of the CNTs grown on the plumbonacrite film is displayed in Figure 3, where 3 major bands related to the multiwall carbon nanotubes (MWCNTs) can be observed. The first one at 1340 cm$^{-1}$ assigned to residual ill-organized graphite, the so-called D-line (D: disorder); a second band at 1588 cm$^{-1}$ called G band that corresponds to the tangential vibration of carbon atoms and a third one at 2690 cm$^{-1}$, which is assigned to the first overtone of the D mode and frequently called G’ mode.[62–65] A fourth signal is detected at 2930 cm$^{-1}$ approximately; this signal is a combination mode of the D and G modes.[58,66] This analysis, in agreement with XRD results, confirms the formation of MWCNTs after the CVD process on the lead and lead oxide material resulting from the transformation of the original plumbonacrite film.

The evolution of the surface morphology of the samples during the CNTs growth process was analyzed by SEM and the results are shown in Figure 4. The SEM images 4a and 4b show the surface of the as-grown plumbonacrite film deposited on a silicon substrate at different magnifications. In these images it is observed the homogeneous plumbonacrite film covering the silicon substrate, constituted by flower-like layered microstructures. These layered structures have size around 10 μm approximately. The images 4c and 4d show the microstructures resulting from the plumbonacrite film introduced to the CVD process, without FeCo solution. The formation of spherical structures of different sizes, from 1 to 10 μm, over the entire substrate is observed. From the XRD analysis, it can be concluded that these microspheres are composed mainly of lead. In the image 4d, it is observed one single sphere which is not completely smooth, its surface presents some roughness in certain areas. This roughness is due to the agglomeration of carbon which decomposes on the surface of the lead sphere during the CVD growth process. In fact, a very small amount of CNTs is observed in this image. After the CNTs growth process, the morphology of the resulting sample of plumbonacrite with FeCo catalyst is shown at different magnifications in images 4e and 4f. In these images, it can be seen that the MWCNTs grew on all the lead spheres covering them completely. The MWCNTs were also formed in the flat region between the lead spheres. These results are in agreement with the previous XRD and Raman spectroscopy results.

Based on the results described above, the entire process of the MWCNTs synthesis can be schematized as shown in Figure 5. First, the FeCo catalyst solution is deposited on the layered structure of plumbonacrite film. Subsequently, when the plumbonacrite film is heated in an inert atmosphere, it decomposes in lead and becomes in the spherical microstructure, retaining the FeCo alloy on its surface. Finally, the contact of acetylene at high temperature with the FeCo external layer produces the growth of the MWCNTs. The resulting nanocomposite films are constituted by MWCNT/Pb/Si, where MWCNT/Pb is the nanocomposite material on Si the substrate.

### 3.2. Photocatalytic results

The disoloration of MB solutions by the interaction with the MWCNT/Pb/Si nanocomposite films in the photocatalytic experiments under sunlight is shown in Figure 6a, which
displays the optical absorption spectra of the MB solution aliquots taken at 60 (solid lines) and 240 min (dashed lines) of each day. It can be observed that the interaction of the MB with the photocatalysts produces a faster decrease on the intensity of the MB absorption bands. Another important aspect that can be observed in absorption spectra of the MB is that during the first day the decrease in the bands of MB is higher than in the second and third days, disappearing at 240 min. In Figure 6b are shown photoluminescence (PL) spectra corresponding to the methylene blue (MB) treated with MWCNT/Pb/Si films under sunlight in a time of 0–240 minutes of irradiation. The PL spectrum of the MB reference solution (0 min) displays a broad emission band at 691 nm, which intensity decreases and maximum position shifts towards shorter wavelengths with increasing exposure time to sunlight irradiation. As can be seen in Figure 6b, the blue shift of the MB emission band is 13 nm after 240 minutes exposed under sunlight. Both features of PL measurements, the decrease in the emission intensity and its blue shift are due to the destruction of the MB chromophoric group by the interaction with CNT/Pb nanocomposite material and activated by sunlight irradiation.

Figure 4. (a) and (b) SEM images of the plumbonacrite film synthesized on the silicon substrate. (c) and (d) Lead spheres obtained from the plumbonacrite film treated at the CNTs growth conditions. (e) and (f) MWCNTs obtained over the lead spheres that contained the FeCo catalyst solution.

Figure 5. Scheme of the MWCNT growth process on the plumbonacrite film.
The discoloration percentage of the MB solutions, of the three days, is displayed in Figure 7a; the photographs of the solutions under sunlight at the times of 60, 120 and 240 minutes are inserted in the graph. During the first day, the MB solution starts with a 62% of discoloration at 60 min and reaches a value of 99% of discoloration at 240 min. In the second day experiment, the discoloration reaches values of 54 and 95% at 60 and 240 min respectively. Finally, in the third day, the discoloration of the MB solution reaches values of 39 and 92% at 60 and 240 min respectively. The plot in Figure 7b, represents the percentages of discoloration of the MB solutions under sunlight using MWCNT/Pb nanocomposite films and pure MWCNTs for comparison. It can be observed that after 240 minutes of solar exposure the solutions treated with MWCNT/Pb show a greater discoloration being almost 100%, and in the case of single MWCNT, an 81% discoloration is obtained after this time.

The data for the determination of the kinetic rate constant for each day are plotted in Figure 8. The larger value of the kinetic rate constant obtained was for the first day reaching a value of $1.18 \times 10^{-2}$ min$^{-1}$ while for the second and third day the values were of $1.05 \times 10^{-2}$ and $8.9 \times 10^{-3}$ min$^{-1}$ respectively. These values are in the range and even higher than other photocatalytic coatings and TiO$_2$-based photocatalytic composite materials reported in previous works.[56,67–73]

The degradation mechanism of the MB on the MWCNT/Pb material is a combination of processes influenced by the photocatalytic capacity of the MWCNT. As can be seen in Figure 7b, MWCNT’s achieved a discoloration of approximately 81% within 240 minutes; this due to the presence of defects in the walls of the nanotubes (by Raman spectroscopy, Figure 3, it was possible to see this condition) which with the absorption of light leads to formation of electron/hole pairs on the surfaces of the highly defective CNTs (1) which are powerful oxidizing (2) and reducing (3) agents, and causes degradation of the MB$^{[35,74,75]}$.

\[
\text{MWCNT} + h\nu \rightarrow h^+ + e^- \quad (1)
\]
\[
\text{OH}^- + h^+ \rightarrow \text{OH}^* \quad (2)
\]
\[
\text{O}_2 + e^- \rightarrow \text{O}_2^- \quad (3)
\]

The second main mechanism is generated as the amount of MB decreases in the solution making it more transparent to sunlight. The increased transparency of the solution allows to sunlight penetrate deeper and induce some photolytic effects, increased by the combination of holes and electrons in the material assisted by the O$_2$ dissolved in water and H$_2$O, respectively, to generate many OH$^-$ [76] causing additional discoloration of the solution$^{[53]}$ by the reactions described by T. Soltani...
treated in the three days; the dashed straight lines correspond to the best linear fit to experimental data in each case.

\[
\begin{align*}
\text{MB}^+ + \text{OH} & \rightarrow \text{MB}^* + \text{OH}^* \quad (4) \\
2\text{OH}^* & \rightarrow \text{H}_2\text{O}_2 \quad (5) \\
\text{MB}^* + \text{O}_2 & \rightarrow \text{MB}^+ + \text{O}_2^- \quad (6)
\end{align*}
\]

where in the reaction (4) highly reactive hydroxyl radicals can be formed through mono-electronic reduction of MB\(^+\) by the hydroxyl ion.[78] Within the same solution then hydroxyl radical species can react with each other’s, reaction (5) and producing \(\text{H}_2\text{O}_2\), which is an important active species in degradation processes. Finally, the oxygen as a radical scavenger can react with MB-radical and form \(\text{O}_2^-\) as another important intermediate species (6); therefore, the photolysis of MB could be preceded via direct reactions of MB with highly reactive radical species that formed in the presence of sunlight irradiation.

The increase in the efficiency of the MWCNT/Pb material compared to the pure MWCNT can be explained by the fact that the Pb support acts as sensitizers and transfer electrons to the MWCNT.[79] This condition allows to the MWCNT to absorb an electron to generate a superoxide radical by adsorbed molecular oxygen. Once this happens, the Pb support remove an electron from the valence band in the MWCNT leaving a hole that react with adsorbed water to form hydroxyl radicals.[80]

4. Conclusions

In this work, we reported the use of plumbonacrite films as support material for the growth of CNTs by the CVD process. The plumbonacrite films were deposited on silicon substrates by using a simple chemical bath method at room temperature, assisted by UV radiation. The results show that during the CNTs growth process, plumbonacrite transforms into spherical lead microstructures on which CNTs grow covering them completely. The CNTs only grew on the plumbonacrite films which were previously impregnated with FeCo catalyst solution. The formation of CNTs was confirmed by XRD, Raman and SEM measurements. The degree of graphitization was calculated based on the Maire and Mering formula, obtaining a value of 21.04%. The nanocomposite MWCNT/Pb films have a large surface area and uniform distribution. The photocatalytic properties of the nanocomposite films were tested in the removal and photodegradation of methylene blue (MB) dye in aqueous solution. The resulting rate of photodegradation of the methylene blue dye by the MWCNT/Pb nanostructures, under sunlight irradiation, strongly depends on supported material, the uniform distribution of the catalyst and the irradiation time on the solutions to be discolored. It is shown that the MWCNT supported in plumbonacrite coatings are sufficiently active for the photocatalytic degradation of the organic compounds, reaching a discoloration rate of almost 100% for a time of 240 minutes. The presence of Pb produces a better electron transfer, which benefits the photodegradation process of the organic compounds. The decolorization efficiency of the methylene blue solutions is shown to be higher than that of pure CNTs, obtaining for this material 81% of discoloration at the same time of irradiation. These results show that the MWCNT/Pb nanostructured composite films could be used in potential applications for the degradation of organic contaminants, with the additional advantage that can be reused in several photocatalytic cycles.

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